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ASSESSMENT OF N_2O IN FLUE GAS

Report No. 89-117-K

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Environmental Science Section
Chemical Research Department

ABSTRACT

An assessment of N_2O levels in the flue gas of coal-fired power plants was undertaken. The role of N_2O in the atmosphere, the present state of knowledge of N_2O in flue gas, and N_2O measurement techniques are discussed. As part of the assessment, measurements of N_2O emissions at Nanticoke TGS were carried out on May 18 and 19, 1988. Average concentrations of 13 and 21 ppmv were measured at the economizer and air heater outlets respectively. N_2O:NO_x molar ratios of less than seven percent were observed. These N_2O:NO_x ratios are substantially less than those presently used to estimate the contribution of N_2O by the utility industry to the global N_2O budget, Kavanaugh (1987). These results are considered preliminary and further sampling is recommended to confirm these numbers.

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35-115-591	837.21	June 9, 1989	89-117-K

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EXECUTIVE SUMMARY

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The mean concentration of nitrous oxide in the atmosphere is presently approximately 300 ppb and is increasing at a rate of about 0.25 percent per year. It is estimated that nitrous oxide will continue to grow due to its long atmospheric lifetime (ie; 150 years in the troposphere, 100 years in the stratosphere). Presently, sources exceed sinks by about thirty percent. The concern over nitrous oxide emissions is based on the fact that N_2O participates in reactions that deplete the ozone layer and is also a greenhouse gas. For these reasons N_2O emissions from power plants may become an environmental concern. As no data on Ontario Hydro's N_2O emissions were available it was decided to undertake an assessment of N_2O in flue gas. The scope of this preliminary assessment was to evaluate the present state of knowledge on N_2O in flue gas, evaluate N_2O measurement techniques, and initiate the measurement of N_2O emissions from Ontario Hydro's generating stations.

High concentrations of N_2O in the combustion gases of electric power stations in the United States have been reported. This has led to the suggestion that combustion represents an important anthropogenic input of N_2O to the atmosphere. More recent evidence in the scientific literature has suggested that some of the previously reported N_2O emissions from combustion may have been overestimated by several orders of magnitude. This has added to the controversy over the anthropogenic N_2O source term.

Preliminary results from measurements of N_2O emissions at Nanticoke TGS indicate N_2O levels lower than those reported in the United States (ie; N_2O:NO_x ratios < 0.07 as compared to values of 0.15 to 0.30 determined in the United States). It is concluded that more data are needed before reliable conclusions regarding the utility industries contribution of N_2O to the global budget can be drawn. It is recommended that further studies be undertaken to quantify Ontario Hydro's N_2O emissions.

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35-115-591	837.21	June 9, 1989	89-117-K

TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	**1**
2.0 N_2O IN THE ATMOSPHERE	**2**
3.0 N_2O IN FLUE GAS	**10**
4.0 N_2O MEASUREMENTS AT NANTICOKE TGS	**15**
4.1 Sampling Techniques	17
4.1.1 Gas Chromatography	18
4.1.2 Tunable Diode Laser Spectroscopy	22
4.2 Sampling Protocol	24
5.0 RESULTS AND DISCUSSION	**27**
6.0 RECOMMENDATIONS	**31**
REFERENCES	**32**
DISTRIBUTION	**last page**

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Environmental Science Section
Chemical Research Department

1.0 INTRODUCTION

Nitrous oxide (N_2O) plays a significant role in two global environmental issues, the greenhouse effect and stratospheric ozone depletion. The role of N_2O in the global warming issue is well understood. Nitrous oxide is one of the many radiatively active trace gases accumulating beyond expected levels in the atmosphere (WMO 1985). These gases absorb infrared radiation emitted from the earth's surface, thereby contributing to a gradual rise in the earth's surface temperature.

N_2O's role in stratospheric ozone depletion is not as clear as in global warming (Tirpak, 1987). N_2O reacts with $O(^1D)$ in the stratosphere to form nitric oxide (NO). The nitric oxide so formed enters into catalytic reactions leading to ozone destruction. However, in the presence of chlorine compounds, resulting from the photo-dissociation of chlorofluorocarbons, the nitrogen from N_2O breakdown can interfere with chlorine-catalyzed destruction of ozone and counter ozone depletion.

It is estimated that anthropogenic activity contributes approximately one-third to the current budget of global N_2O emissions (Weiss, 1981). Of this one-third, combustion processes are thought to account for 85% with the utility sector through oil and coal burning estimated to be responsible for 53% of the combustion total (Kavanaugh, 1987). In other words, the utility sector has been identified as contributing roughly 15% of the total global emissions of N_2O.

These estimates are based on a small number of published measurements of N_2O emissions from combustion of fossil fuels (Kramlich et al, 1988). Recent studies of N_2O measurement techniques and N_2O formation mechanisms have cast some doubt on the validity of the existing data base of N_2O emissions from coal combustion. The existing data

indicate that N_2O emissions from coal fired power plants can approach twenty to thirty percent of the NO_x emissions, on a molar basis. However, emissions of N_2O fluctuate from one power plant to another (Hao et al, 1987). At present, the fundamental mechanisms leading to N_2O formation in combustion and the factors which influence N_2O concentrations in flue gas are not well understood. Therefore, to ensure accurate assessments of past and future trends in atmospheric N_2O, more measurements of N_2O and those factors which influence its formation are required.

This report presents results of a preliminary assessment of N_2O in flue gas. The specific goals of this definition phase of the work program were to select and develop methods to sample N_2O in flue gas, and to carry out preliminary measurements at Nanticoke TGS to initiate the development of an N_2O emission factor. N_2O had not been previously measured in Ontario Hydro's power plants. Based on the experience gained in this initial phase, recommendations for further work to characterize Ontario Hydro's N_2O emissions are made.

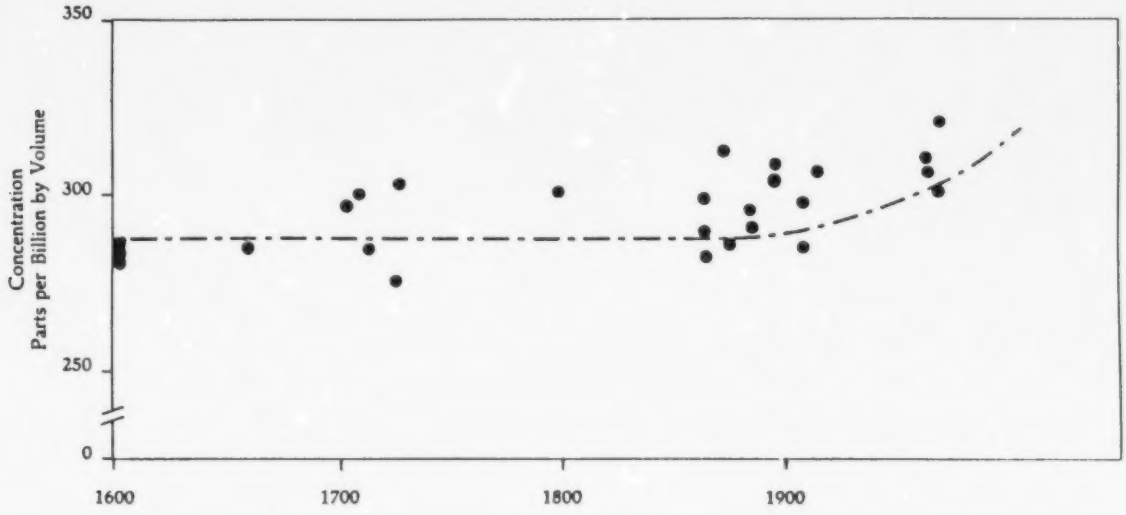
Section 2.0 of this report presents a brief summary of the present scientific information on N_2O and its accumulation in the atmosphere. Section 3.0 discusses N_2O in flue gas, highlighting measurements made to date and the speculation on its formation. Section 4.0 outlines the techniques and methods employed during the Nanticoke TGS tests. Section 5.0 presents and discusses the results of these tests and Section 6.0 tables recommendations for future work.

2.0 N_2O IN THE ATMOSPHERE

Scientific evidence is sufficient to demonstrate that ambient levels of nitrous oxide are increasing in the atmosphere. Figure 1, (Pearman et al, 1986) illustrates this from ice core measurements. The ice core data show that atmospheric concentrations of N_2O were reasonably constant at about 280 ppbv from 1600 to 1900. After the industrial revolution N_2O levels steadily increased. The present mean global concentration of N_2O is approximately 300 ppbv (WMO, 1985).

Estimates of the rate of increase of tropospheric nitrous oxide vary from 0.2 to 0.4 percent per year (Khalil et al, 1983). Larger rates of increase appear to be observed in the northern hemisphere than in the southern hemisphere. Based on the data of Pearman et al (1986) and atmospheric measurements of N_2O by Weiss (1981), Weiss constructed a model predicting tropospheric N_2O concentration to the Year 2050, Figure 2. Although some of Weiss's assumptions regarding global sources and sinks for N_2O data are questionable, measurements are in agreement with the model (Hao et al, 1987). It is generally concluded that if the present imbalance between sources and sinks remains the N_2O concentration will increase in the future. The model of Weiss (1981) suggests the N_2O concentration will exceed 360 ppbv by the year 2050.

Figure 1: Estimated Atmospheric Concentration of N_2O (Parts per Billion by Volume)



N_2O concentrations measured in ice cores formed during the last 400 years.

Source: Pearman et al., "Evidence of Changing Concentrations of Atmospheric CO_2, N_2O, and CH_4 from Air Bubbles in Antarctic Ice," *Nature*, volume 320, 1986.

Figure 2: Predicted tropospheric N_2O concentrations from 1860 to 2050. (source Hao et al, 1987)

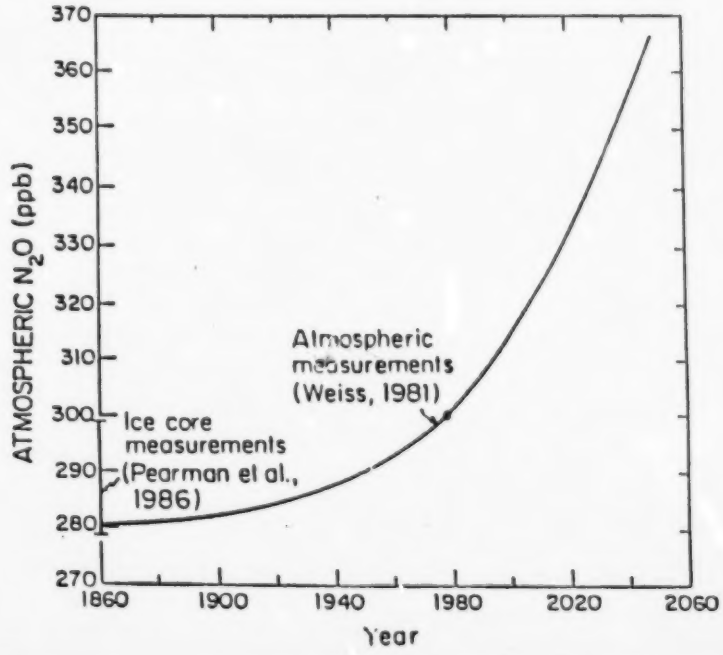


Table I, (Tirpak, 1987), tabulates the atmospheric lifetimes of N_2O and other trace gases associated with the greenhouse and stratospheric ozone issues. The estimated tropospheric lifetime of N_2O is 150 years. N_2O is inert in the troposphere, the only known sink being transport to the stratosphere (Table 2). This process is slow relative to the present estimate of the N_2O source strength. It is estimated that the source of N_2O exceeds the sink by more than 30% (Weiss, 1981).

Table II and Figure 3 present a summary of N_2O sources. From Figure 3 it can be seen that natural sources account for approximately two thirds of the ambient N_2O loading. Although all the mechanisms for N_2O production in soils are not well understood, measurements show emissions from soils represent two thirds of the natural component (WMO, 1986).

From Figure 3 it can be seen that anthropogenic sources account for nearly one-third of the ambient loading. Therefore this component is important in respect to the estimated thirty per cent imbalance between source and sinks. It is also the source component which could be considered as controllable (Lanier et al, 1987).

It is currently thought that combustion processes account for most of the anthropogenic component (ie: 85%, Table II). Through the burning of coal and oil the utility industry is estimated to be responsible for approximately 15% of the anthropogenic source.

Faced with an increasing atmospheric N_2O concentration, what are the potential effects? Figure 4 illustrates those trace gases which have absorption bands in the atmospheric window (7 to 13 microns). Note that N_2O absorbs in three regions of the atmospheric window. Trace gases which absorb in the atmospheric window trap outgoing infrared radiation. Because of this, the majority scientific opinion is that the accumulation of these gases will lead to a gradual warming of the earth's surface beyond normally expected levels. Figure 5 illustrates the projected cumulative surface warming effect from each of these radiatively active trace gases based on the model of Ramanathan et al (1985). These projections show by the year 2030, increases in N_2O at historically observed rates will cause an increase in the global equilibrium temperature of 0.1 degrees centigrade.

Increasing concentrations of N_2O are also of concern because of its role in stratospheric ozone depletion. Depletion of the stratospheric ozone layer allows penetration of harmful ultraviolet radiation (UV-B) to the earth's surface. N_2O by itself in the stratosphere undergoes destruction primarily by photolysis.

A small fraction of N_2O reacts with $O(^1D)$ to form either NO or N_2 and O_2 (with a branching ratio of about unity). The NO then reacts in a catalytic cycle leading to the net destruction of ozone, ie

TABLE I

ATMOSPHERIC LIFETIMES OF TRACE GASES

Compound	Formula	Lifetime (years)
CFC-11	CCl_3F	75*
CFC-12	CCl_2F_2	111*
CCF-22	$CHClF_2$	20#
CFC-113	$C_2Cl_3F_3$	90#
Carbon tetrachloride	CCl_4	50*
Methyl chloroform	CH_3CCl_3	6.5*
Halon 1211	CF_2ClBr	25#
Halon 1301	CF_3Br	110#
Methane	CH_4	11*
Nitrous Oxide	N_2O	150*

*Source: World Meteorological Organization. Atmospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change. World Meteorological Organization, Geneva, Switzerland, 1986.

#Source: National Academy of Sciences. Causes and effects of changes in stratospheric ozone. National Academy Press, Washington, DC, 1984.

TABLE II

GLOBAL SOURCES AND SINKS OF NITROUS OXIDE (N_2O)

ATMOSPHERIC BURDEN (10^6 tons as N)	1500
SINKS + ACCUMULATION (10^6 tons N per year)	14.0 ± 3.5
1. stratospheric photolysis + reaction with $O(^1D)$	10.5 ± 3.0
2. accumulation (0.7 ppb per year)	3.5 ± 0.5
SOURCES (10^6 tons N per year)	
1. Natural	9.7
Tropical soil emissions	7.4 ± 4.0
Non-tropical soil emissions	0.1 - 0.5
Oceans	2.0 ± 1.0
2. Anthropogenic	5.5
Combustion	
Utility coal and oil	2.12
Industry coal and oil	1.64
Households coal and oil	0.24
Tropical biomass	0.6
Non-tropical biomass	0.1
Fertilized agricultural lands	0.8

Source: Table is adapted from McElroy and Wofsy, as reported in World Meteorological Organization. Atmospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change. World Meteorological Organization, Geneva, Switzerland, 1986. Combustion emissions are computed based on 1975 source estimates presented in Kavanaugh, M. Estimates of future CO, N_{2O} and NO_x emissions from energy combustion. Atmospheric Environment, 21(3): 463-468, 1987.

Total Natural: ≈0.3 Tmol/yr (from stratospheric removal models assuming no other sinks)

Oceans: ≈0.1 Tmol/yr (from mean oceanic supersaturation of ≤4% and radon calibrated exchange models)

Terrestrial: ≈0.2 Tmol/yr (by difference, includes soil sources and sinks)

Anthropogenic: ≈0.14 Tmol/yr (from observed rate of increase and box model calculations)

Note: 1 Tmol = 10^{12} g moles

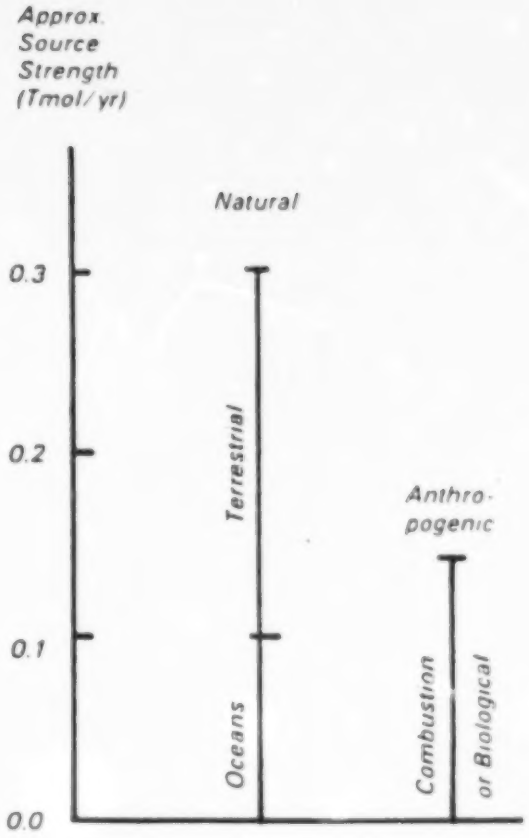


Figure 3: *Estimated N_2O global fluxes (Source: R. F. Weiss, Scripps Institution of Oceanography, 1986).*

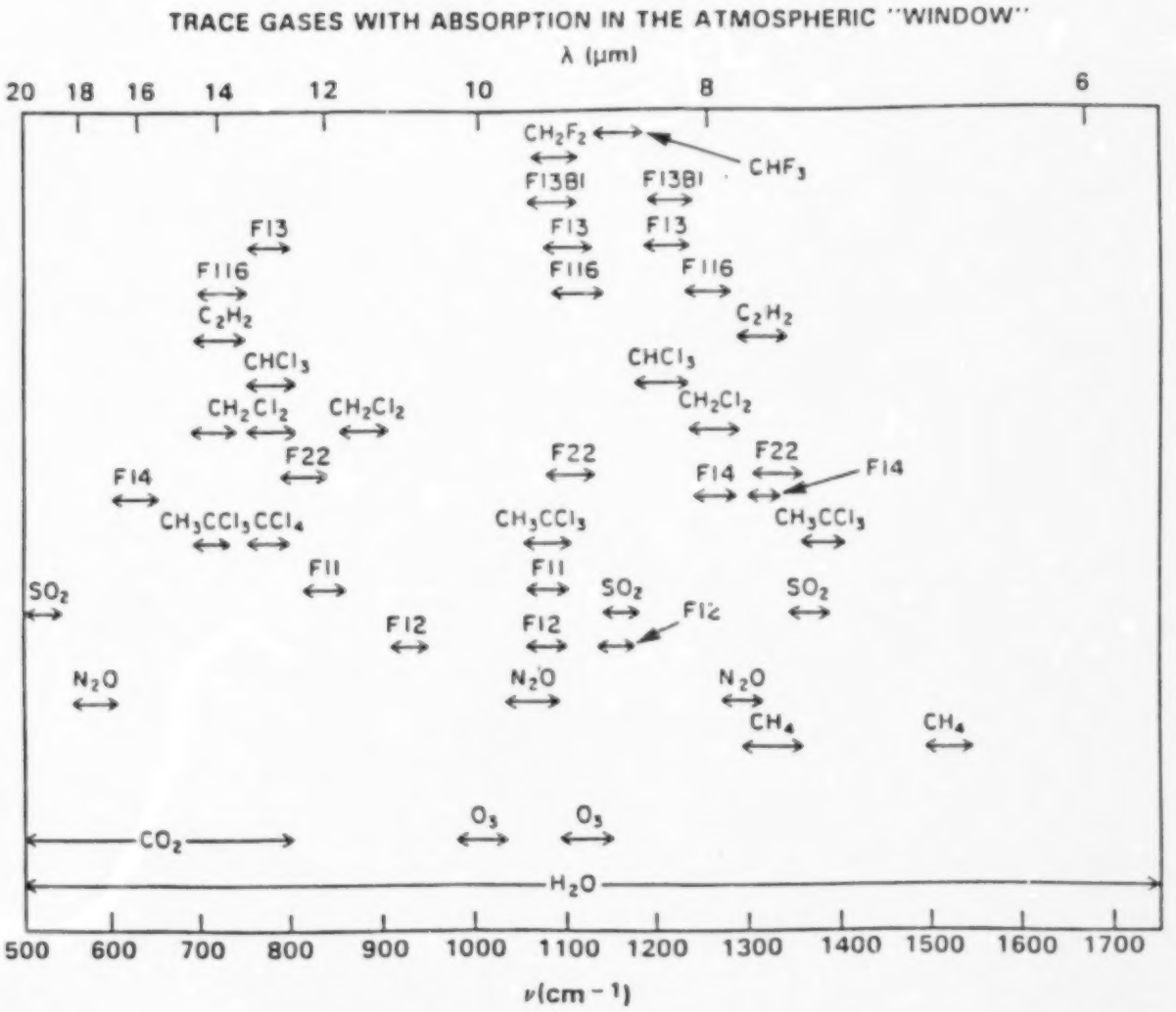


Figure 4: Spectral locations of the absorption features of various trace gases. The spectral region between 7 to 13 μm is referred to as the atmospheric "window."

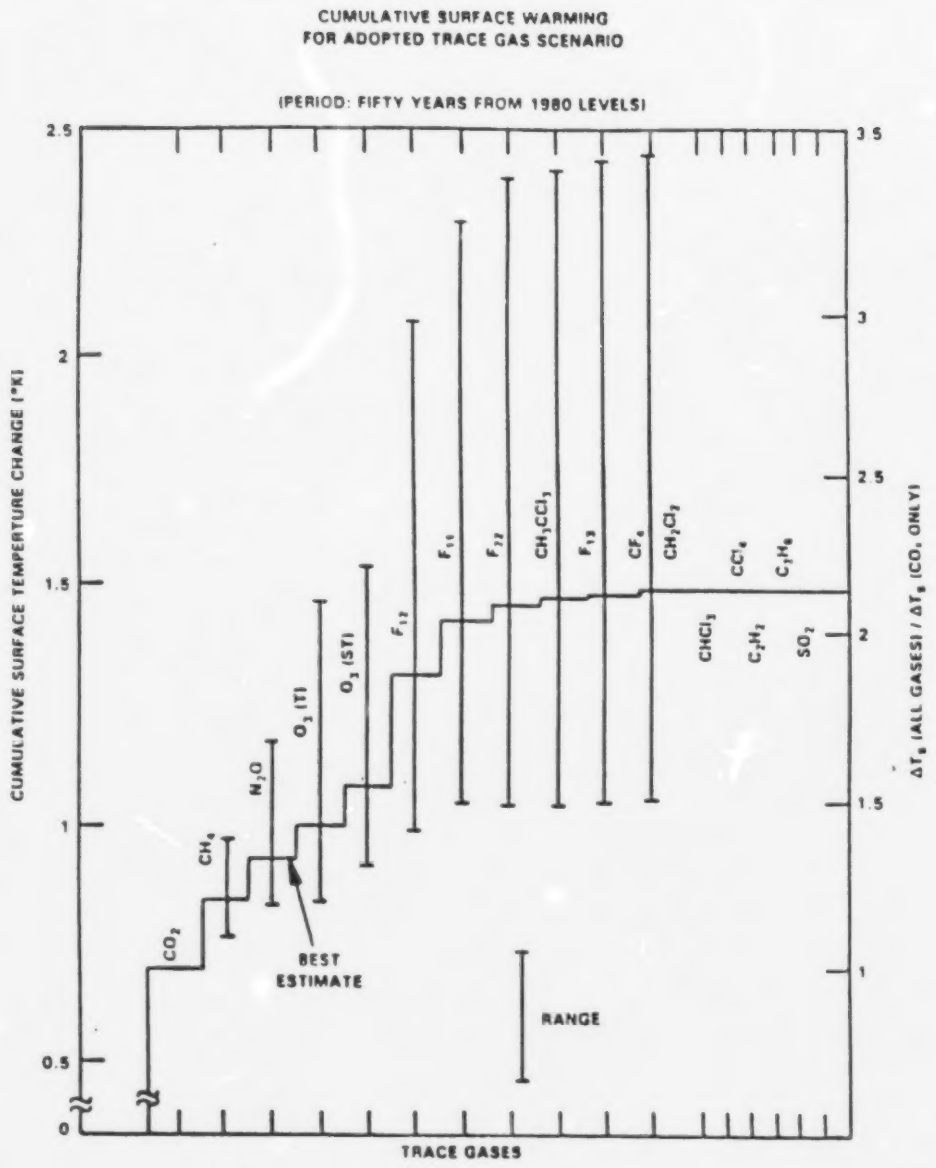


Figure 5: Projected equilibrium global warming for the year 2030 for central scenario of trace gas concentrations.

Note that other trace gases contribute twice as much to the warming as CO_2. Model estimates are for a sensitivity of 2 degrees Centigrade for doubled CO_2 concentrations. Source: Ramanathan, V. et al. Trace gas trends and their potential role in climate change. Journal of Geophysical Research 90(D3): 5547-5566, 1985.

$$N_2O + O(^1D) \text{ ----> } 2NO$$
$$\text{ ----> } N_2 + O_2$$

followed by

$$NO + O_3 \text{ -----> } NO_2 + O_2$$
$$\underline{NO_2 + O \text{ -----> } NO + O_2}$$
$$O_3 + O \text{ -----> } 2O_2$$

However, Tirpak (1987), points out that in some cases N_2O can counter ozone depletion. That is, in the presence of high concentrations of chlorine compounds, NO_x interferes with the chlorine-catalyzed destruction of ozone. NO_x produced from stratospheric N_2O destruction also has interactions with HO_x chemistry (Wuebbles, 1988).

Although it is important to recognize the potential impact of increasing N_2O on global atmospheric chemistry and climate, it is equally important to maintain a perspective on these data. In particular, Wuebbles (1988) warns that the evaluation of the relationship between energy activities and emissions of N_2O are primitive. Despite this, claims are made that combustion processes account for 85% of the anthropogenic source. Certainly more studies of the influence of trace chemicals in the atmosphere on climatic processes are required, however, it is important to better quantify N_2O sources and formation/destruction mechanisms before a satisfactory evaluation of N_2O's role in global environmental problems can be made.

3.0 N_2O IN FLUE GAS

A typical flue gas composition is shown in Table III. To quote Kramlich et al (1988), "The discovery that combustion systems can generate N_2O and indeed are major sources of N_2O came as something of a surprise to the technical community". Kramlich offers an excellent review of the present state of knowledge on the N_2O formation/destruction mechanisms during combustion. The reader is referred to his review for a detailed discussion of the mechanisms associated with N_2O formation in flue gas. A brief summary of N_2O in flue gas is offered below.

TABLE III

TYPICAL FLUE GAS COMPOSITION

O_2	3-4%
CO_2	10-15%
NO_x	500 ppm
CO	50-100 ppm
SO_2	1000-1500 ppm
Hydrocarbons	200-300 ppm (?)

Figure 6 presents an overview of the present understanding of the formation mechanism of N_2O in flue gas, EER (1988). N_2O production has been shown to be clearly related to fuel nitrogen (ie: more N_2O is formed from the combustion of coal and oil than from natural gas), however the amount of N_2O formed appears to be very sensitive to how the fuel is burned. The direct thermal production of N_2O is considered to be a very minor process. At peak flame temperatures (ie: >1500°C), N_2O is formed but short lived due to consumption by; $N_2O + H = N_2 + OH$. Thus it is thought that most of the N_2O emission is a result of N_2O precursors (eg; NH_4, HCN, nitrogenous char) which escape the flame zone and react subsequently at locations where temperatures are lower. In the case of nitrogenous char there are two possible pathways, either by direct heterogeneous oxidation or by HCN formation and subsequent oxidation to N_2O.

In the case of the other precursors, both direct and non-sequential pathways are speculated to contribute to formation, depending on burn conditions. Additionally, there is accumulating evidence that N_2O formation occurs in post furnace systems in the presence of NO_x, SO_x, and water. From this summary it is clear that N_2O production is quite sensitive to factors such as coal type, combustion system type, load, and how the coal is burned. Thus N_2O emissions can vary substantially from one power plant to another.

The amount of data on N_2O concentrations in flue gas are very limited. Those data that are available cover only a narrow range of combustion scenarios (Hao et al, 1987; Weiss and Craig, 1976; Castaldini et al, 1983; Beer et al, 1981; and Marland et al, 1983). In efforts to estimate the contribution of combustion to the global N_2O budget, these data have been correlated with NO_x to determine an average value of N_2O/NO_x. Figure 7 illustrates one such effort based on data from Castaldini et al (1983), also published in Hoa et al (1987). Figures 8 and 9 present additional data compiled by Lanier et al (1987), and Kramlich et al (1988), respectively. Note that these data sets (ie: Figures 7, 8, & 9) are not mutually exclusive. If these measurements are correct the data suggests that NO_x and N_2O are correlated to the first order and that N_2O could be estimated as twenty to thirty percent of NO_x. Extrapolation of this ratio worldwide balances the global budget of tropospheric N_2O increase. A recent publication by Kavanaugh (1987) has, based on these data, used an N_2O emission factor of 22% of NO_x for coal and oil combustion. Kavanaugh constructs estimates of future CO, N_2O, and NO_x emissions from energy combustion and suggests that future global N_2O and NO_x combustion emissions are likely to increase unless there is new regulation.

At a recent EPA workshop on N_2O (Kramlich et al, 1988) several differing viewpoints were expressed on the N_2O/NO_x correlation and the ability to estimate the global N_2O contribution from combustion based on NO_x emissions. One view was that although the correlation has no fundamental basis it still may be a useful qualitative guide to estimate the anthropogenic N_2O source term. Another view was that the correlation was purely accidental, and that there were insufficient data to construct a statistically meaningful sample of the worlds combustion systems. The third position was that the database is not yet adequate to extract any conclusions.

MECHANISM OVERVIEW

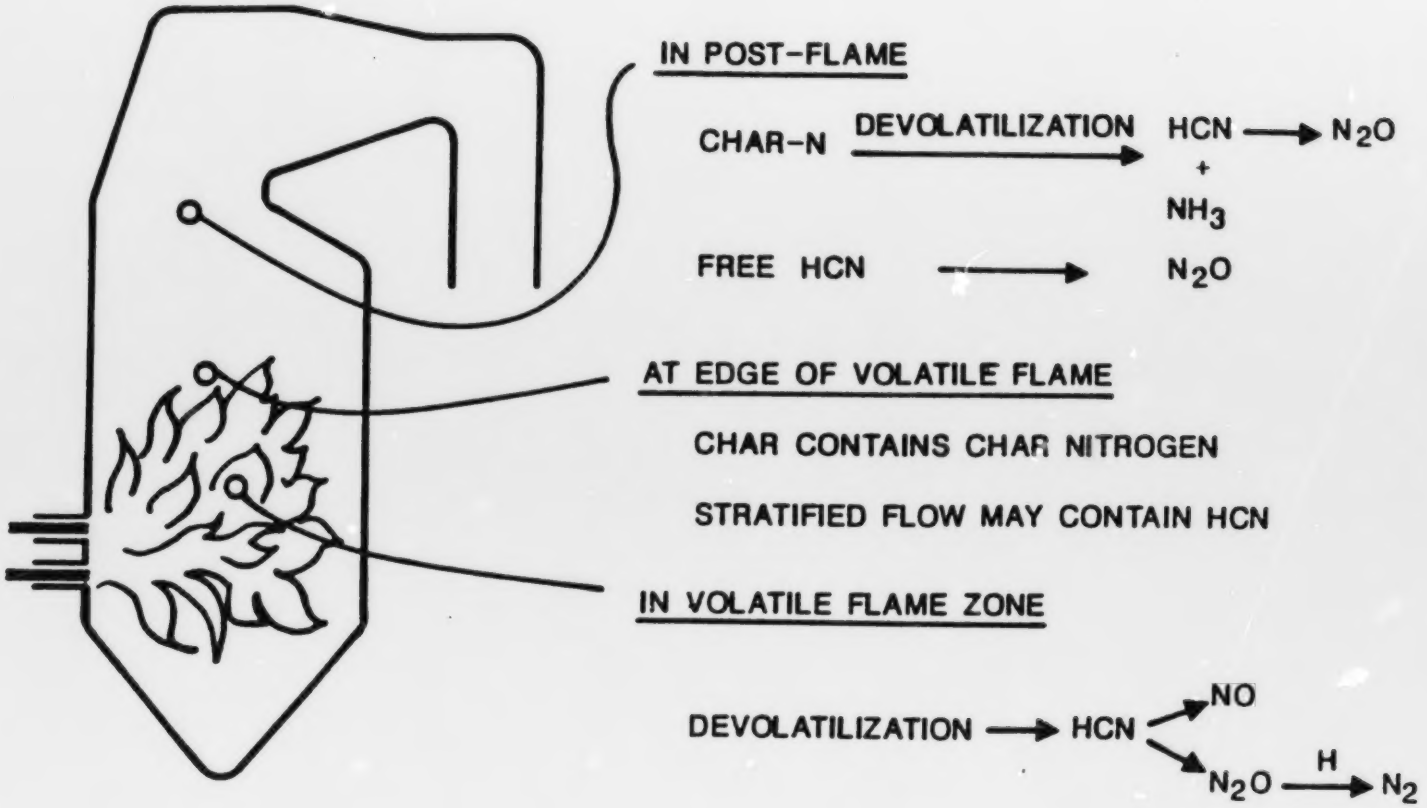


FIGURE 6

Overview of N_2O formation mechanisms
(source: EER, 1988)

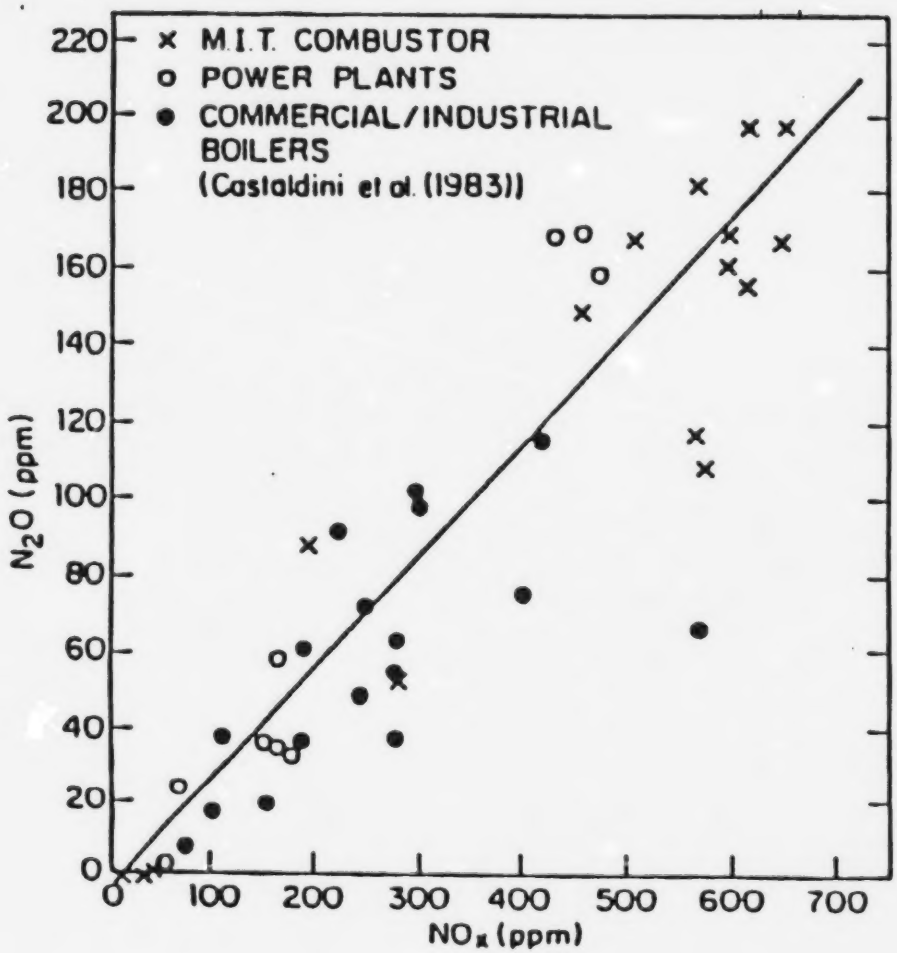


FIGURE 7

Field and pilot-scale data correlation of NO_x against N_2O. (reproduced from Hao et al, 1987)

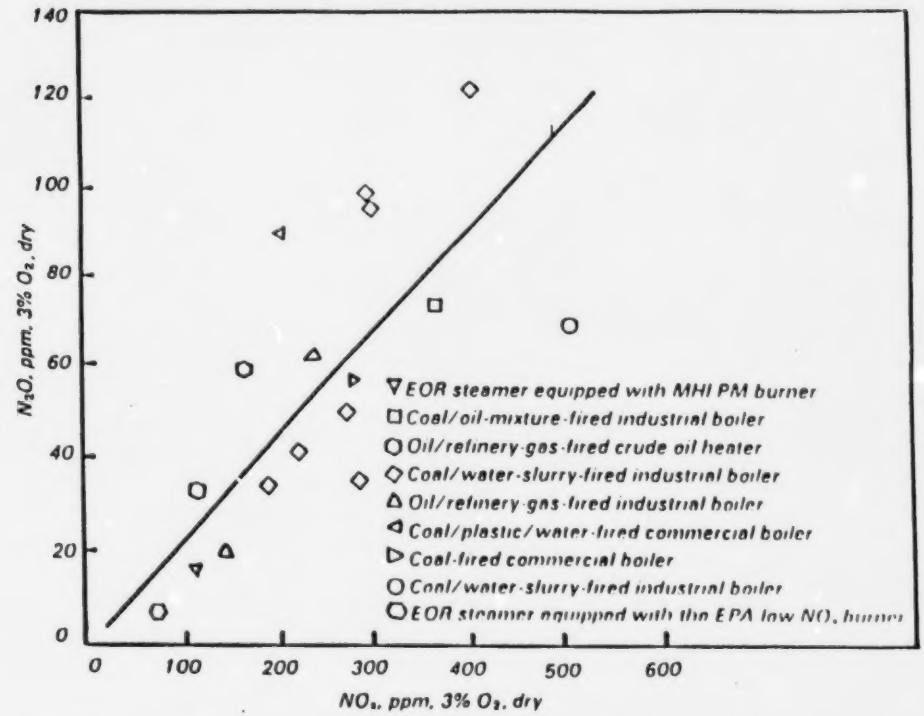


Figure 8: *N_2O emissions from combustion sources as a function of NO_x emission (Source: Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner. Volume 1. Technical Results, EPA/600/7-86/003a (NTIS PB 86-159837), February 1986).*

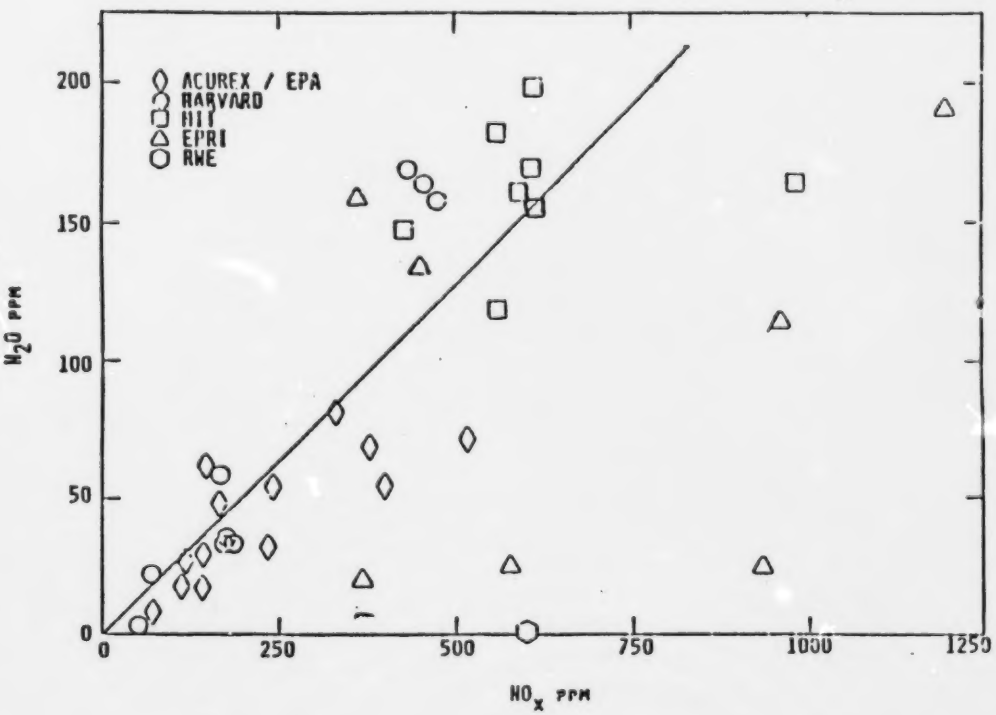


Figure 9: Field and pilot-scale data correlation of NO_x against N_2O.

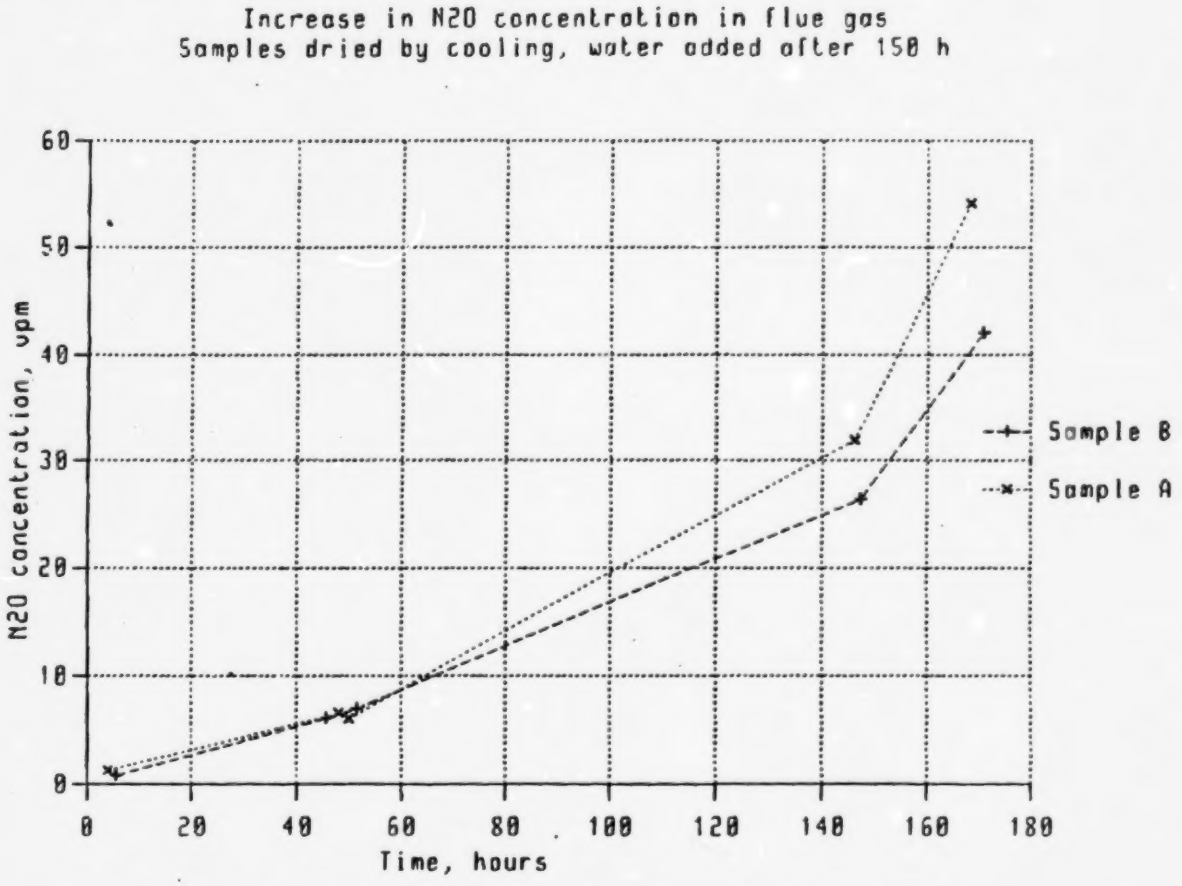
The latter viewpoint has been reinforced recently by Muzio and Kramlich (1988) whose work has shown that flask sampling approaches to N_2O measurement can produce errors of several orders of magnitude depending on the time between sample collection and sample analysis. Rapid N_2O formation can occur if the sample contains NO, water and SO_2, all common products of combustion. Figure 10, (A. Cocks, CEGB, 1988, Personal Communication) illustrates how N_2O concentration can increase with time in a flue gas sample (ie: dry conditions) and how rapid the concentration increase is in the presence of water vapour. This also casts doubt on data from those techniques which sample hot flue gas in real time, where there is the possibility of N_2O formation occurring in sampling lines and apparatus from condensed water. It appears, therefore, that there is no data upon which to adequately assess whether N_2O from combustion is a major component of the global N_2O budget. In fact, the Science News article describing the work of Muzio and Kramlich quotes Joe Levine from NASA as saying, "This fundamentally revises our thinking. If the emission factor in the chimney is reduced by a factor of 100, then coal burning, on a global scheme, does not become a major source of N_2O." Levine goes on to say that past studies have underestimated the amount of land burned each year. Moreover, his group and others have shown that land burning creates N_2O not only by combustion but also by stimulating soil microbes, which produce N_2O for months after a fire. This controversy over the emission factor for N_2O from coal combustion points to the need for measurements which will unambiguously quantify N_2O in flue gas. It also suggests that these measurements ideally need to be obtained near the chimney exit.

The Central Electricity Generating Board in Great Britain are presently researching techniques to measure N_2O in flue gases from coal-fired boilers. They are also investigating the detailed kinetics and mechanisms of the NO, SO_2, and H_2O interaction leading to N_2O formation. Some preliminary measurements of N_2O in flue gas obtained by gas chromatograph and infra-red absorption techniques are shown in Table IV below (Cocks, 1988.)

There are insufficient data here to draw any conclusions, however these data do indicate $CO2:N_2O$ ratios substantially lower than those used by Weiss and Craig (1976) to estimate the N_2O emission factor used to balance the global budget.

4.0 N_2O MEASUREMENTS AT NANTICOKE TGS

Preliminary testing of the N_2O sampling techniques and protocols was carried out at Nanticoke TGS on May 18 and 19, 1988. These dates were selected for the N_2O measurements in order to align with tests of boiler performance being undertaken by the Fuel Physics and Performance Department, (FPPD), Central Production Services Division, (CPSD). Alignment with FPPD facilitated access to sampling ports and additional data on flue gas composition. In addition to obtaining N_2O measurements, the purpose of these tests were to gain experience with the sampling techniques in a station environment and to determine an appropriate experimental approach for obtaining N_2O data. The following sections describe the sampling techniques, the methods employed and the data obtained at Nanticoke TGS.



Increase in nitrous oxide concentration in two samples of flue gas. The samples were dried to a dew point of approximately 278 K at the time of sampling. Water sufficient to saturate the samples was added after 150 h.

FIGURE 10

Growth of N_2O in a flask sample of flue gas.
(source: A. Cocks, CEGB, personal communication)

TABLE IV

SUMMARY OF CEGB MEASUREMENTS OF N_2O IN FLUE GAS

Station	Boiler Type	Unit	Date	Load	No. of Samples (GC)	N_2O Concentration (ppm) GC (ppm)	NDIR (ppm)	Ratio CO_2:N_2O
A	Wall fired	4	9.8.1983	455	4	32±2.0**	-	
		1	9.8.1983	300	4	28±3.3**	-	
A	Wall fired	1 (low NO_x)	19.4.1988				13±3	8230
		2	19.4.1988		-	-	16±4	8500
B	Corner fired	1 (low NO_x)	9.12.1987 - 12.12.1987	450-490	20	2.4±1.3	2.6±0.4	50000
		3	10.12.1987 - 11.12.1987	440-495	16	4.5±2.0		

** These samples were cooled to approximately 276°K while sampling and were stored for 24-48 h before analysis. The results almost certainly over estimate the true N_2O con centration in the flue gas.

4.1 Sampling Techniques

At present, there are no methods available to routinely measure/monitor N_2O emissions in flue gas. Laboratory techniques and highly skilled personnel are presently required to undertake N_2O measurement. Many questions surround the existing data base of N_2O emission measurements, consequently there is a need to develop instrumentation/techniques to reliably quantify N_2O emissions.

The three techniques which are presently under development or in use to measure N_2O emissions are gas chromatography using electron capture detection (GC/ECD), broad band IR absorption, and diode laser IR absorption. Most all of the measurements of N_2O in flue gas obtained to date have been by GC/ECD based techniques alone. EPRI is currently sponsoring a research program to apply broad band IR absorption based techniques to measure N_2O (Kramlich, et al, 1988). To successfully apply broad band IR techniques to the measurement of N_2O in flue gas requires considerable effort to identify and eliminate interferences from other IR absorbing gases found in flue gas. The EPRI method in its

present state of development has an error in the range of 3-7 ppm N_2O. For sources with low levels of N_2O, application of this method would not be appropriate.

The Environmental Science Section (ESS), has considerable experience with GC/ECD and diode-laser-based, gas monitoring techniques. In consideration of this and the error involved with the broad band IR technique it was decided to focus attention on the GC/ECD and diode laser techniques for this initial evaluation.

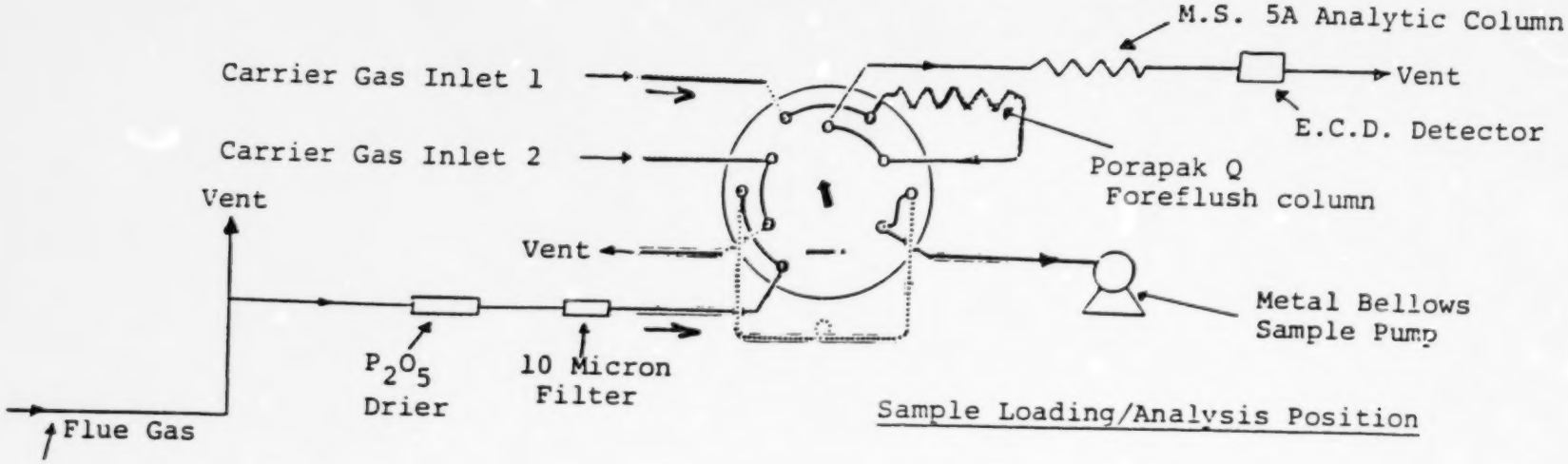
4.1.1 Gas Chromatography

There are several opinions on the best GC/ECD approach for the measurement of N_2O (Kramlich et al, 1988; EER, 1988). If N_2 is the chosen as the carrier gas extreme care must be exercised to avoid interferences from CO_2. The ECD measures N_2O by dissociative capture of a low energy electron by N_2O, that is: $N_2O + e^- \rightarrow N_2 + O^-$. The O^- ion, however, can react further; $O^- + N_2O \rightarrow NO^- + NO$, $NO^- + M \rightarrow NO + e^- + M$. This reaction sequence releases the captured electron therefore decreasing the amount of ECD signal for a given amount of N_2O. The presence of CO_2 would lead to $CO_2 + O^- + M \rightarrow CO_3^- + M$ which competes with NO^- formation, increasing the sensitivity of the ECD and thus requiring correction for the amount of CO_2 in the sample. Furthermore, there is some question as to what effect the purity of the N_2 carrier gas has on the ECD. The sensitivity of the ECD depends on the trace impurities in the carrier gas (ie; O_2). Apparently, the use of truly pure N_2 results in reducing the ECD sensitivity to zero.

These problems can be avoided by the use of Ar-CH_4 as the carrier gas and using a procedure described in Kramlich et al (1988) involving the use of ascarate to check for CO_2 interference.

For the Nanticoke N_2O measurements a Varian Model 3400 Gas Chromatograph equipped with a Nickel-63 electron capture detector was used. The carrier gas was high purity nitrogen and was passed through a purification train consisting of an oxygen and molecular sieve trap. All delivery tubing to the instrument was stainless steel. A schematic diagram of the arrangement is shown in Figure 11. It will be shown later that the N_2-based GC/ECD technique used here provided adequate sensitivity to measure N_2O at ppmv levels.

The gas sampling valve was a Valco multi-functional ten-port valve with stainless steel body and Valcon "S" core. The valve was fitted with 0.159 cm zero volume fittings, and was heated inside the gas chromatograph oven. An external secondary oven, heated to 70°C, contained the foreflush column. Figure 11 illustrates the flow path through the valve in both the load and inject positions. The sample was further dried using a P205 drier. Particulate material was removed using a 10 micron filter.



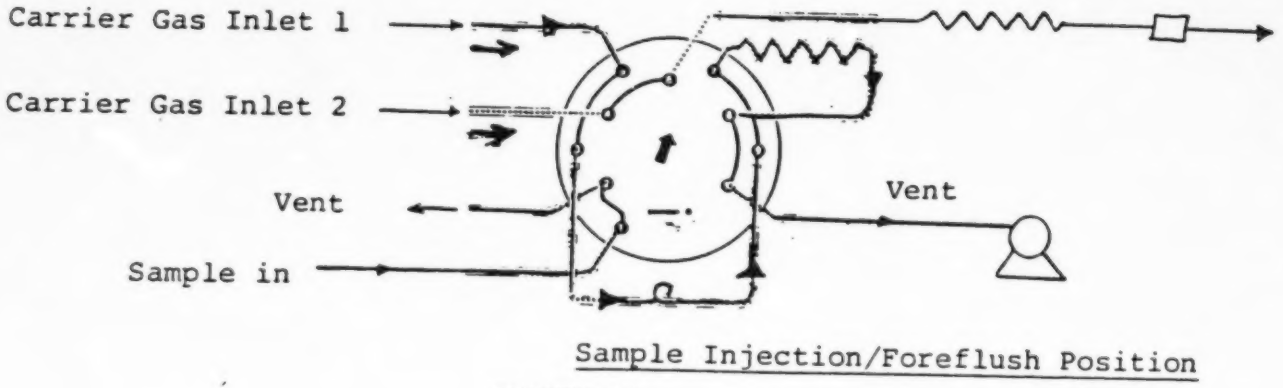


FIGURE 11

SCHEMATIC DIAGRAM OF SAMPLING/CHROMATOGRAPHY SYSTEM

Figure 11

The foreflush column used to separate the N_2O from oxygen and other components was a 1.8 m x 0.318 cm OD stainless steel column packed with Porapak Q, 60/80 mesh operating at 70°C. Figure 12 lists the relative retention times of N_2O and other components on Porapak Q. The analytical column for the final separation of N_2O from other residual components was a 2.5 m x 0.318 cm column packed with molecular sieve 5A, 60/80 mesh operating in the GC oven at 100°C.

A dynamic dilution system was used to generate trace gas mixtures of N_2O in a synthetic flue gas mixture. Pure CO_2, O_2, SO_2, CO, N_2 and primary standards of 1% NO, 1% NO_2, and 1% N_2O were mixed using Tylan FC280 mass flow controllers. All connections were stainless steel throughout the system and all flows were standardized to NTP (101.3 KPa, 25°). Concentration ranges achieved are shown in Table V.

TABLE V

CONCENTRATION RANGES ACHIEVED IN SYNTHETIC FLUE GAS MIXTURE

Oxygen	3-4%
Carbon Dioxide	10-15%
Nitric oxide/nitrogen dioxide	500 ppm
Carbon Monoxide	10-100 ppm
Sulphur Dioxide	1000-1500 ppm
Nitrous Oxide	1-500 ppm

The detector was operated at 250°C, the foreflush column at 70°C and the analytic column at 100°C. With the use of a ten port valve in this system the optimum carrier gas flow rates and foreflush time were determined by the following procedure. A known concentration of N_2O in the synthetic flue gas mixture was drawn from the dynamic dilution system through the 25 mL sample loop on the ten port valve. After adequate flushing, the sample was then injected into the foreflush column, the valve switched to the sample loading position at a preselected time and the chromatograph recorded. By varying the carrier gas flow rates and foreflush times the response to N_2O was plotted against calculated concentration. Gross deviations from linearity indicated premature foreflush valve switching. The gas chromatograph was optimized for fast response. The optimum parameters are shown in Table VI.

FIGURE 12

RELATIVE RETENTION TIMES ON PORAPAK Q

O_2	---------	0
NO	---------	0.08
CH_4	---------	0.12
CO_2	----------	0.35
N_2O	---------	0.48
C_2H_2	---------	0.67
C_2H_4	---------	0.74
C_2H_6	---------	1.00
H_2O	---------	1.36
H_2S	---------	1.51
COS	---------	2.55
C_3H_6	---------	3.52
SO_2	---------	3.61
C_3H_8	---------	4.00

TABLE VI

OPTIMIZED GC PARAMETERS

Foreflush	30 s
Carrier Gas Flow 1	40 mL/min
Carrier Gas Flow 2	40 mL/min
N_2O retention	65 s after injection
Injection Frequency	approx 180 s

Quadruplicate calibration runs were carried out using the optimum values shown in Table VI. The system was calibrated in the range 1 to 500 ppm N_2O in synthetic flue gas. The repeatability of measurements was determined at each concentration and the data plotted. The derived precision (95% confidence limit) is shown in Table VII. The overall repeatability achieved by the system was approximately 10%.

TABLE VII

DERIVED PRECISION OF GC CALIBRATION

N_2O (ppm)	Precision (%)
500	3.4
250	4.6
100	5.3
50	5.9
10	6.7
5	7.6

4.1.2 TUNABLE DIODE SPECTROSCOPY

The diode laser IR absorption technique offers the potential of unambiguous measurement of N_2O in flue gas with high accuracy and sensitivity. The diode laser emits monochromatic light within a narrow bandwidth of the order of 10^{-4} cm^{-1}. This feature combined with a low pressure sampling approach avoids the interference problems associated with broad band IR techniques. A typical detection limit for N_2O at low pressure (ie: 50 mb) is 2 ppbv (Reid et al, 1978). The diode laser approach also offers the advantage of real time fast response measurement. Response time is primarily limited by gas exchange times in

the absorption cell. In detecting N_2O concentrations on the order of ppmv, response times of 10 to 20 Hz could easily be achieved.

The principal disadvantages of tunable diode laser (TDL) gas monitoring have been cost and difficulty of operation. Until recently, laser diodes have required cooling to liquid helium temperatures and complex optical and signal processing to achieve optimum trace gas detection. However, with the introduction of single mode high temperature lasers (ie; 77 K), and advanced signal processing technology, improvements in system costs and ease of use are now possible.

As part of a study of dry deposition processes the Environmental Science Section have developed a fieldworthy TDL gas monitor based on the helium cooled diode lasers and are presently developing a system based on the new liquid nitrogen type of laser. Although the present development is directed towards operation of the diode laser in conditions associated with the atmospheric environment, it is possible that with little modification the TDL could be applied to the measurement of N_2O in a generating station environment. As part of the N_2O measurement program it was decided to test the present liquid helium cooled TDL during the Nanticoke tests to gain experience with the difficulties of operating such an instrument in a station environment.

A schematic of the TDL instrument used at Nanticoke TGS is shown in Figure 13.

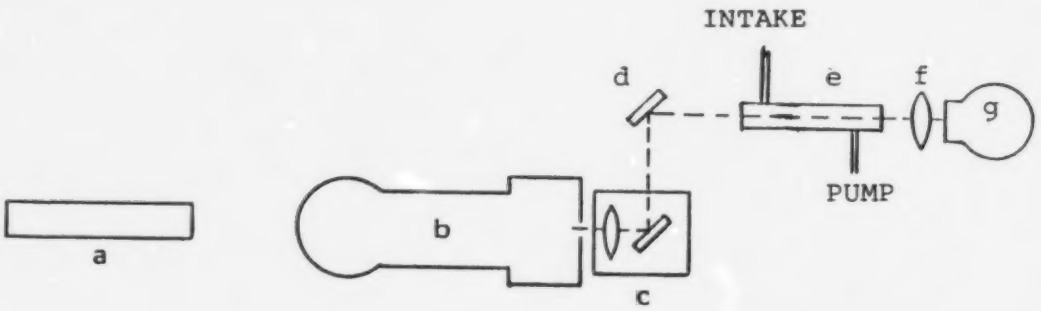


FIGURE 13

Schematic of diode laser instrument used at Nanticoke. (a) HeNe Laser for alignment, (b) diode laser coldhead, (c) Collimating lens on XYZ Mount, (d) Mirror, (e) Absorption Cell, (f) Focusing Optics, (g) HgCdTe IR Detector.

The laser light emerges from the helium cold head (b) and is collimated via (c) into a 20 cm long, 100 cc absorption cell (E). The light from the absorption cell is then focused (f) onto the 1 mm^2 element of a HgCdTe detector (g). The principal of TDL trace gas

detection is the absorption of the infrared laser beam over the path through the gas sample cell. In this case the N_2O gas concentration is directly related to the extent of absorption by the following relationship:

$$\frac{Io-I}{Io} = \alpha NL$$

Where

- I is the measured laser intensity (Detector)
- Io is the laser intensity that would be detected with no absorbers present
- α is the absorption coefficient
- N is the concentration of the absorbers
- L is the path length.

This relation is valid for $\alpha NL << 1$.

The instrument will therefore have a linear response for total absorptions of a few percent. For N_2O measurement the instrument was calibrated by flowing known N_2O concentrations through the sample cell. Typical precisions for the prepared N_2O mixtures are shown in Table VII. Several known samples were mixed, bracketing the expected measurement range. Linear instrument response facilitated direct determination of sample N_2O concentration.

For this instrument configuration, the detection threshold and the sensitivity for N_2O were estimated to be approximately 0.1 ppmv, and 0.5 ppbv respectively, and instrument response was approximately 5 Hz.

4.2 SAMPLING PROTOCOL

Nanticoke TGS has eight 500 MW coal-fired units. The boilers were manufactured by B&W and are a wall fired design. The N_2O measurements were made in conjunction with FPPD during an air heater leakage evaluation of unit 2. Tests were carried out over two days, May 18 and 19, 1988. During the testing the unit was burning a blend (1.5% sulfur content) of US and western Canadian bituminous coal. Unit 2 utilizes staged combustion to lower NO_x emissions. In the course of the performance evaluation FPPD obtained measurements of CO_2, SO_2, NO, NO_2, and O_2. The flue gas samples were taken from two locations, the air heater outlet and the economizer outlet. Figure 14 locates the two sampling sites, and Figure 15 illustrates the grid of sampling ports in the ducts at these sites. Long, medium, and short designations shown on Figure 15 refer to sampling location in the duct. A cleanup cart was located near the sampling sites to remove water and particulates from the flue gas. The samples were then pumped via lengths (approximately 100 m) of 3/8-in. diameter plastic tubing to the gas monitoring instrumentation. At this point a flow bypass of approximately 4 L/m was provided by FPPD for N_2O sampling.

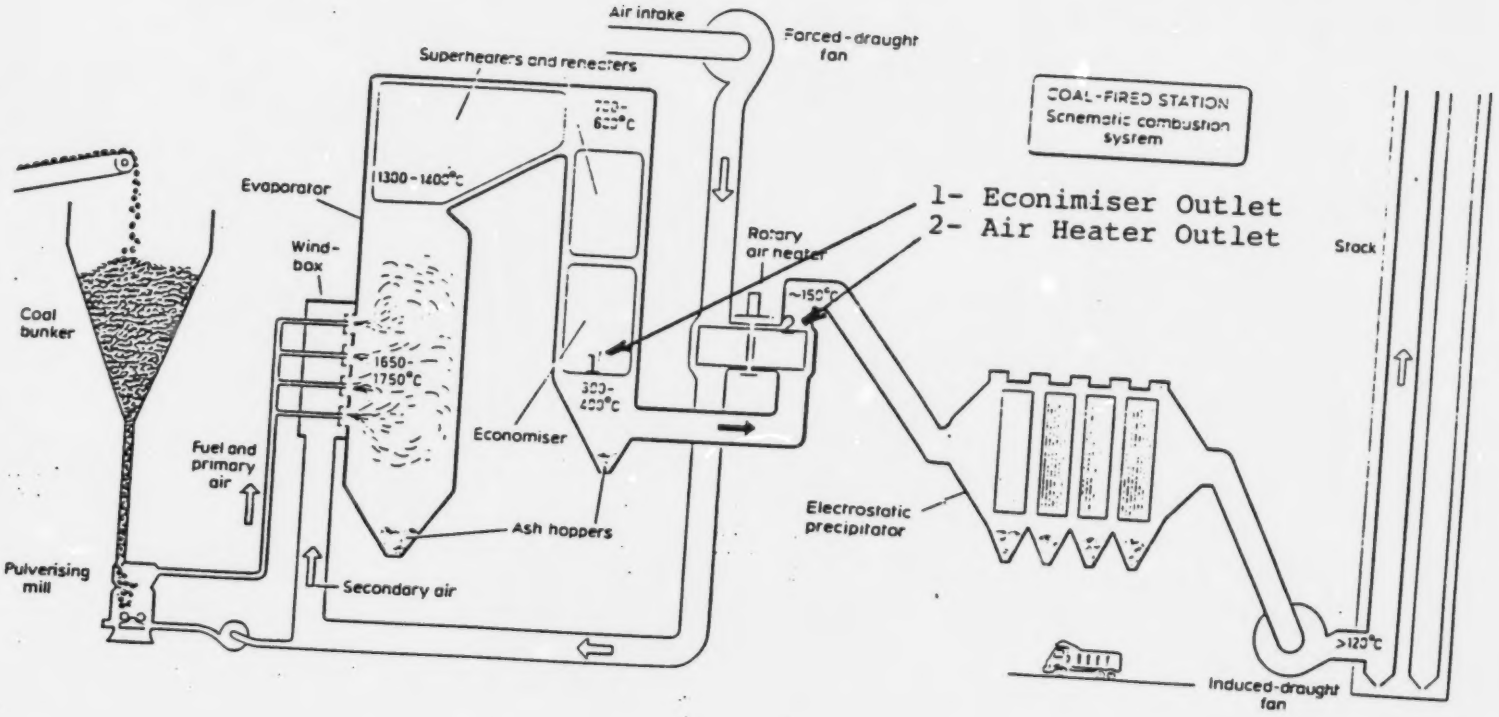
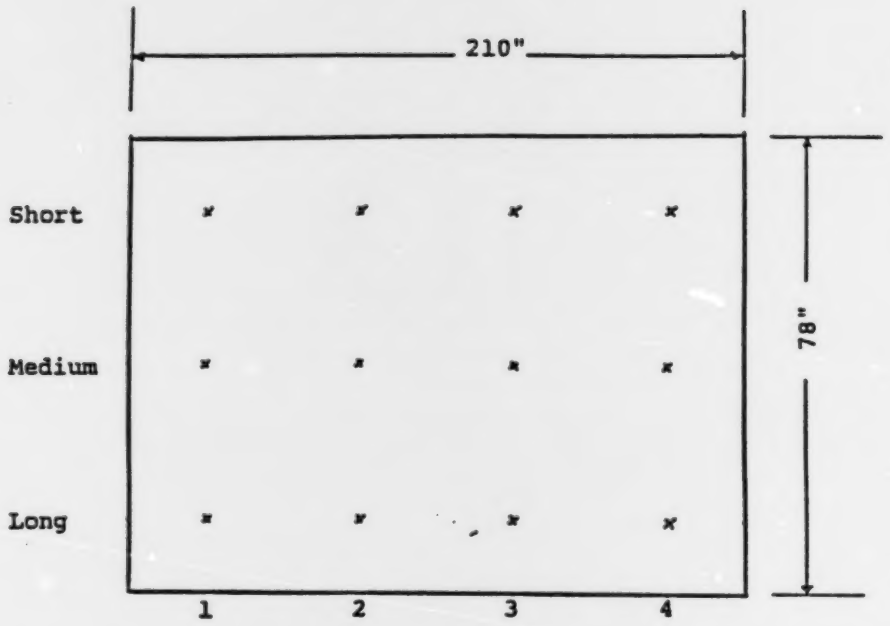
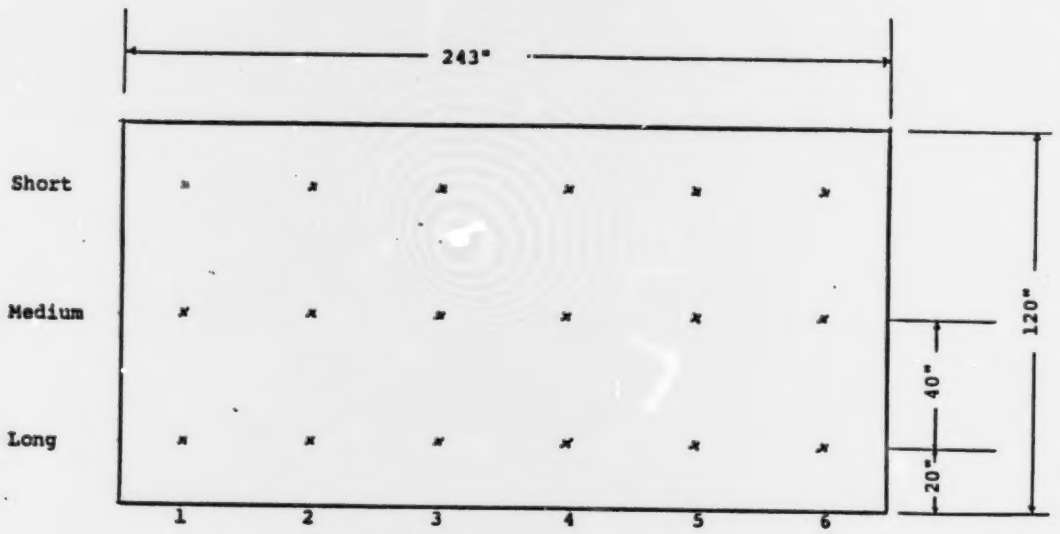


FIGURE 14

Combustion system layout showing N_2O sampling locations



NANTICOKE TGS
ECONOMIZER OUTLET



NANTICOKE TGS
PRIMARY AIR PREHEATER
OUTLET DUCT

FIGURE 15

Sampling port detail on economizer and air heater outlet ducts.

As discussed in the last section the flue gas sample was again dried and particulates removed in this bypass line.

Test conditions were prescribed by the FPPD performance evaluation. On May 18, 1988 unit 2 was operated at full load (ie: 500 MW) during the sampling. Both morning and afternoon tests were performed. On May 19, the unit was operated at 300 MW and only a morning test was carried out. The FPPD apparatus facilitated sampling individual ports as shown in Figure 15. Typically, an experiment would involve obtaining, in sequence, measurements at each port of a chosen row, and then a 2-min average at each port. For example, if the economizer outlet short row of ports were selected, the sample would be flushed through position 1 for 2 min, and the average measurement for the next 2 min. recorded. When measurements were being obtained of position 1, position 2 would be in a flush mode. Measurements would continue in sequence across the duct. Analyzer response and switching time (approximately 2 min.) dictated the total test time. A test of this type would take approximately ten minutes on the economizer outlet duct and fifteen minutes on the air heater outlet site (6 ports per row).

During the morning period of May 18, time allowed for tests to be performed on all rows of ports on both the economizer and air heater outlet ducts. These same ducts were sampled again during the afternoon of May 18. Additionally, over the period 13:00 to 14:30 on this day, continuous sampling of N_2O was done on port 3 of the medium port row of the economizer outlet duct. On the morning of May 19, a special test was arranged whereby unit 2 would operate at a load of 300 MW. Sampling was performed, in this case, on the row of medium ports on both the economizer, and air heater outlet ducts. The results of these tests are presented and discussed in the next section.

5.0 RESULTS AND DISCUSSION

Considerable experience with the GC/ECD and TDL techniques and with N_2O sampling methodologies in the station environment were gained during the Nanticoke tests. Also, some preliminary measurements of N_2O in real time at two points in the combustion system were obtained. Table VIII summarizes these N_2O measurements. The data shown in Table VIII were are all obtained by the GC/ECD technique. No data were obtained by the TDL technique due to instrumentation problems. The nature of these difficulties are discussed later. It should be emphasized that the data shown in Table VIII are preliminary in nature, requiring confirmation through further sampling.

On average, the measurements indicate values of 13 ± 2.3 ppm at the economizer outlet sampling site and 21 ± 3.5 ppm at the air heater outlet sampling site. Direct comparison of these results to other N_2O data is difficult as sampling methods, conditions, and location in the combustion system differ considerably. However, the CEGB data shown in table 4 show N_2O levels for wall fired boilers (low NO_x included) to be approximately 13 to 16 ppm. Figure 16 shows data published by Hao et al (1987), on N_2O concentrations as a function of distance from the furnace front wall for staged and unstaged combustion. N_2O concentrations for the comparable staged combustion data show values on the same order as those measured at Nanticoke TGS.

TABLE VIII

SUMMARY OF N_2O MEASUREMENTS[1] AT UNIT 2, NANTICOKE TGS

Date	Load	Location		O_2 %	NO_x ppm	N_2O ppm	Avg N_2O ppm
May 18, am	500 MW	Economizer Outlet	1[2]	3.5[3]	468[3]	15.7[3]	
			2	3.3	460	10.1	
			3	3.2	461	11.1	
May 18, pm	500 MW	Economizer Outlet	1	3.4	487	16.4	
			2	3.3	479	11.6	
			3	3.2	473	10.6	
May 18 13:09 to 14:24	500 MW	Economizer Outlet 12 sample average	2	---	---	13.3 ±2.7	13 ± 2.3
May 19, am	300 MW	Economizer Outlet	2	4.3	407	11.7	
			2	5.0	442	15.1	
			2	4.4	409	14.6	
May 18, am	500 MW	Air Heater Outlet	1	8.0	472	20.2	
			2	8.2	468	19.5	
			3	8.8	472	24.5	
May 28, pm	500 MW	Air Heater Outlet	1	8.7	486	22.5	
			2	8.2	495	17.6	21 ± 3.5
			3	8.1	486	16.5	
May 29, am	300 MW	Air Heater Outlet	2	10.5	417	24.0	
			2	10.5	411	26.7	

[1] These are preliminary results, to be confirmed through further sampling

[2] Numbers refer to the probes used for sampling the ducts (1-short, 2-medium, 3-long)

[3] Values are the average of several readings, corrected to 3% excess oxygen

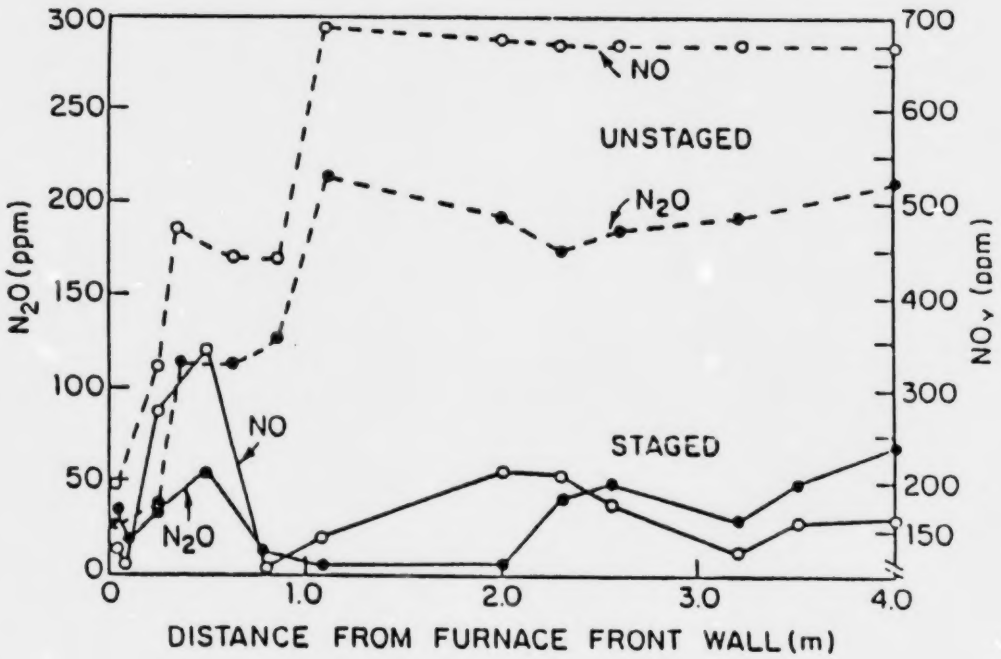


FIGURE 16

N_2O concentrations in staged and unstaged combustion conditions. (source: Hao et al, 1987)

Calculation of average N_2O:NO_x ratios from the data shown in table 8 show a range of 3 to 5 percent. These numbers are substantially lower than the 22 percent value used by Kavanaugh (1987) to estimate the contribution of N_2O from combustion to the global N_2O budget. As well, recent studies by Muzio et al (1989), Linak et al (1989) and unpublished data from a survey of N_2O emissions from Canadian Utilities carried out by Energy and Environmental Research Corporation indicate N_2O levels less than 10 ppm and no correlation between N_2O and total NO_x.

The data in Table VIII also indicate, on average, an increase in the N_2O concentration from the economizer outlet sampling site to the air heater outlet location. This result may not be significant in view of the sampling procedure and the paucity of data. One possible explanation for this observation however, is N_2O formation between the two sampling locations due to NO_x + SO_x + H_2O interaction and/or SO_x deposition in the ducting. Further investigation of this irregularity is required.

Considering the controversy over the published data on N_2O concentrations in flue gas and the few results presented here it is clear that more reliable data are needed before conclusions about the utility industries contribution of N_2O to the global budget are drawn. Future efforts to quantify N_2O emissions must quantify controlling variables such as flue gas composition, and combustion conditions. As well, sampling closer to the point of emission, (ie; stack exit) will allow a more accurate assessment of the N_2O emission to the atmosphere.

The Nanticoke tests also provided experience with the two monitoring techniques and with sampling methodologies in the station environment. No major difficulties were experienced with the performance of the GC apparatus in the station environment. ECD sensitivity was adequate to detect N_2O in flue gas at ppm levels. Although the GC was optimized for fast response (ie: 180 s turnaround) this may not be sufficient for investigations of N_2O formation in the combustion system. Suggested improvements to the GC/ECD technique would involve evaluation of different column packings to increase oxygen retention beyond nitrous-oxide and carbon dioxide. This would enable the GC to be configured with a single column operating on a backflush technique as opposed to the foreflush system now being employed. A backflush configuration of this type would provide much faster measurements and possibly better resolution.

Although no data were obtained by the TDL technique some valuable insights into the necessary characteristics for a TDL-based N_2O instrument were gained. The instrument configuration used at Nanticoke experienced several problems. Sixty cycle noise pickup in the electronic components (current source, temperature controller, lock-in-amplifier, all designed for laboratory service) was severe in the station environment. As a result, tuning the laser to an N_2O absorption line was difficult. Holding the laser on a line was even more difficult. Vibrations, including those at sixty cycle are more prevalent than expected in the station environment. This affected the optical components, greatly reducing the instrument signal-to-noise ratio. These effects combined rendered the instrument incapable of N_2O measurement during the Nanticoke test period. Instrument size and calibration procedure were also inappropriate for operation in a TGS.

Despite the difficulties encountered at Nanticoke with the helium-cooled laser system it is felt that the problems can be overcome by a revised instrument design. Presently a compact, rugged design based on the liquid nitrogen cooled lasers, fibre optics, real time calibration and improved electronic signal processing is being tested. When field testing of this design is complete it is proposed to use the new TDL system in conjunction with the GC/ECD approach in further studies to quantify N_2O emissions.

The station environment is a particularly difficult one in which to undertake the measurement of emissions. It is clear that many more measurements will be required at Nanticoke to adequately quantify N_2O emissions. Sampling procedures need to be improved to minimize losses and or gains in the long runs of sampling tube required. More attention to flue gas preconditioning, sampling protocol, monitoring of combustion system conditions and flue gas components is required.

6.0 RECOMMENDATIONS

Recent data has shown substantially lower values of N_2O in flue gas (ie: <10 ppm) than were measured in the past. It is felt that N_2O emissions at these levels will not have a significant impact on the environment.

However, the paucity of data, and the questions surrounding accurate measurement of N_2O and its formation and growth in flue gas suggest further measurements to better quantify N_2O emissions from Ontario Hydro facilities are needed.

It is recommended that further efforts to quantify Ontario Hydro's N_2O emissions involve the use of both the GC/ECD and the new TDL instrument when development has been completed. The TDL technique offers the advantage of unambiguous detection of N_2O without interference effects from other components in the flue gas. Further efforts to quantify N_2O emissions will also require a more comprehensive experimental approach to determine the factors controlling N_2O formation rates. This may involve studies of N_2O formation in the stack and plume as well as laboratory studies of N_2O formation processes.

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